Contrasted Effects of Methylbenzaconine and Benzaconine.

Methylbenzaconine is from three to four times more toxic towards rabbits and guinea-pigs than benzaconine, and from twice to thrice as toxic towards frogs (*R. temp.* and *R. esc.*). In mammals, slight salivation, retching movements, and muscular tremor are characteristic effects of the former, but dyspnœa, ataxia, and paresis are also seen after benzaconine. Of the two, methylbenzaconine is distinctly less depressant towards the heart. Slowing of the pulse and want of sequence of ventricular upon auricular action occurs after both, but is a much earlier symptom after benzaconine, which causes more disorder in the motor mechanism. On the other hand, the intracardiac vagus is put out of function more readily by methylbenzaconine. Death after either poison is rarely preceded by spasm. Neither of the two compounds cause any local irritation in frogs, but methylbenzaconine produces active fibrillation in the muscles, to which it gains access and develops a complete curare-like action much more prominently than does benzaconine, the heart continuing to beat strongly. Benzaconine, in dose sufficient to cause such an effect at the periphery, acts disastrously upon the circulation. In partial poisoning by methylbenzaconine the characteristic rapid failure of the intramuscular motor nerves on stimulation is well marked, but the subsequent recovery on resting, so characteristic of benzaconine, has not been observed.

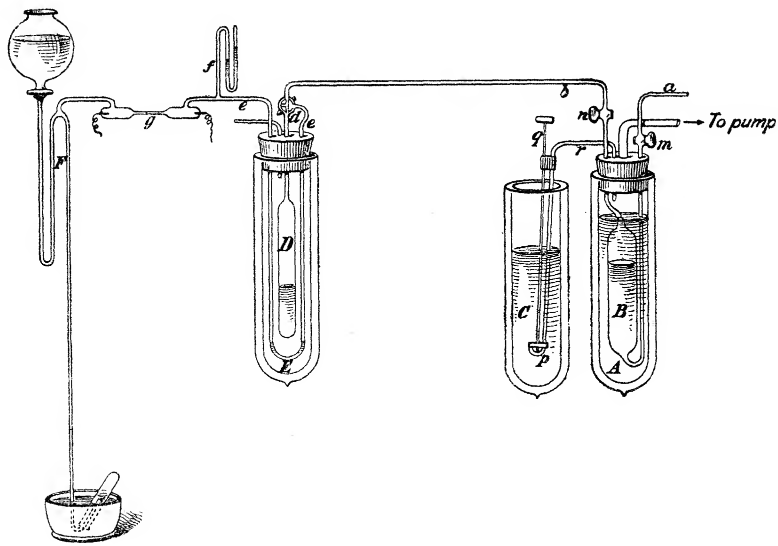
"On the Separation of the Least Volatile Gases of Atmospheric Air, and their Spectra." By G. D. LIVEING, M.A., Sc.D., F.R.S., Professor of Chemistry in the University of Cambridge, and JAMES DEWAR, M.A., LL.D., F.R.S., Jacksonian Professor in the University of Cambridge, Fullerian Professor of Chemistry, Royal Institution, London. Received June 15,—Read June 20, 1901.

Our last communication to the Society* related to the most volatile of the atmospheric gases, that which we now beg leave to offer relates to the least volatile of those gases. The former were obtained from their solution in liquid air by fractional distillation at low pressure, and separation of the condensible part of the distillate by cooling it in liquid hydrogen. The latter were, in the first instance, obtained from the residue of liquid air, after the distillation of the first fraction, by allowing it to evaporate gradually at a temperature rising only very slowly. The diagram, fig. 1, will make the former process intelligible.

* 'Roy. Soc. Proc.,' vol. 67, p. 467.

A represents a vacuum-jacketed vessel, partly filled with liquid air, in which a second vessel, *B*, was immersed. From the bottom of *B* a tube, *a*, passed up through the rubber cork which closed *A*, and from the top of *B* a second tube, *b*, passed through the cork and on to the rest of the apparatus. Each of these tubes had a stopcock, *m* and *n*, and the end of tube *a* was open to the air. A wider tube also passed through the cork of *A* and led to an air-pump, whereby the

FIG. 1.



pressure above the liquid air in *A* was reduced, and the temperature of the liquid reduced by the consequent evaporation. To keep the inner vessel, *B*, covered with liquid, a fourth tube, *r*, passed through the cork, and its lower end, furnished with a valve, *p*, which could be opened and closed by the handle *q*, dipped into liquid air contained in the vessel *C*. As the pressure above the liquid in *A* was less than that of the atmosphere, on opening the valve *p* some of the liquid air was forced through *r* into *A* by the pressure of the atmosphere, and in this way the level of liquid in *A* maintained at the required height.

Since *B* was maintained at the temperature of liquid air boiling at reduced pressure the air it contained condensed on its sides, and when the stopcock *n* was closed and *m* opened, more air passed in through the open end of *a*, and was in turn condensed. In this way *B* could be filled completely with liquid air, the whole of the most volatile gases being retained in solution in the liquid.

The tube, *b*, passing from the top of *B*, was connected with a three-

way stop-cock d, by which c could be put in communication with the closed vessel, D, or with the tube e, by which also D and e could be connected. The tube e passed down nearly to the bottom of the vacuum jacketed vessel E, and out again through the cork; and on to a gauge f, and through a sparking tube g to a mercury pump F. The stopcock n being still closed, the whole of the apparatus between n and the pump, including the vessel D, was exhausted, and liquid hydrogen introduced into E. The three-way cock d was then turned so as to connect c with D, and close e, and then n opened. B was thereby put in communication with D, which was at a still lower temperature than B, and the gas dissolved in the liquid in B, along with some of the most volatile part of that liquid, distilled over, and the latter condensed in a solid form in D. When a small fraction of the liquid in B had thus distilled, the stop-cock d was turned so as to close the communication between D and c, and open that between D and e. Gas from D passed into the vacuous tubes, but in so doing it had to pass through the portion of e which was immersed in liquid hydrogen, so that condensible matter carried forward by the stream of gas was frozen out.

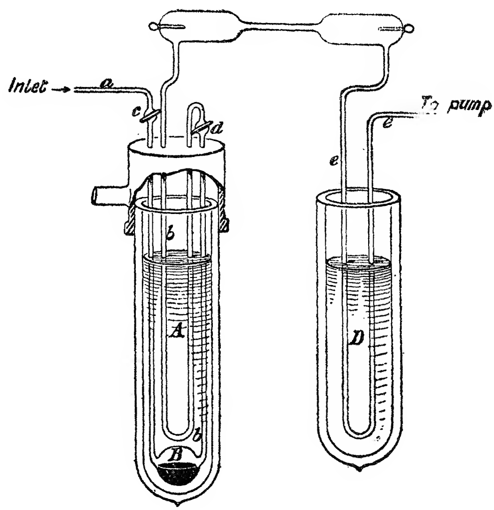
For separating the least volatile part of the gases, the vessel E, with its contents, was dispensed with, and the tube c made to communicate directly with that connected with the gauge, sparking tube, and pump; and generally several sparking tubes were interposed between the gauge and pump, so that they could be sealed off successively. The bulk of the liquid in B consisted of nitrogen and oxygen. These were allowed gradually to evaporate, the temperature of B being still kept low so as to check the evaporation of the gases less volatile than oxygen. When a great part of the nitrogen and oxygen had thus been removed, the stopcock n was closed, and the tubes partially exhausted by the pump, electric sparks passed through g, and the gases examined spectroscopically. More gas was then evaporated from B, and the spectroscopic examination repeated from time to time.

The general sequence of spectra, omitting those of nitrogen, hydrogen, and compounds of carbon, which were never entirely removed by the process of distillation alone, was as follows: The spectrum of argon was first noticed, and then as the distillation proceeded the brightest rays, green and yellow, of krypton appeared, and then the intensity of the argon spectrum waned, and it gave way to that of krypton until, as predicted by Runge, when a Leyden jar was in the circuit, the capillary part of the sparking tube had a magnificent blue colour, while the wide ends were bright pale yellow. Without a jar the tube was nearly white in the capillary part, and yellow about the poles. As the distillation proceeded, the temperature of the vessel containing the residue of liquid air being allowed to rise slowly, the brightest of the xenon rays began to appear, namely, the green rays

about λ 5420, 5292, and 4922, and then the krypton rays soon died ou and were superseded by the xenon rays. At this stage the capillary part of the sparking tube is, with a jar in circuit, a brilliant green and is still green, though less brilliant, without the jar. The xenon formed the final fraction distilled.

Subsequently an improved form of apparatus was used for the fractionation. It is represented in fig. 2. A gasholder containing the

FIG. 2.



gases to be separated, that is to say, the least volatile part of atmospheric air, was connected with the apparatus by the tube *a*, furnished with a stopcock *c*. This tube passed on to the bulb *B*, which in turn communicated through the tube *b* and stopcock *d* with a sparking tube, and so on through the tube *e*, with a mercurial pump.* Stopcock *d* being closed and *c* opened, gas from the holder was allowed to pass into *B*, maintained at low temperature, and there condensed in the solid form. Stopcock *c* was then closed and *d* opened, and gas from *B* allowed to pass into the exhausted tubes between *B* and the pump. The tube *e* was partly immersed in liquid air in order to condense vapour of mercury, which would otherwise pass from the pump into the sparking tube. The gas passing into the sparking tube would, of course, have a pressure corresponding to the temperature of *B*, and this was further ensured by making the connecting tube pass through the liquid in which *B* was immersed. The success of the operation of separating all the gases which occur in air and which boil at different

* The Sprengel pump shown in figure is simply diagrammatic.

temperatures depends on keeping the temperature of B as low as possible, as will be seen from the following consideration :—

The pressure p, of a gas G, above the same material in the liquid state, at temperature T, is given (approximately) by the formula

$$\log p = A - \frac{B}{T},$$

where A and B are constants for the same material. For some other gas G' the formula will be

$$\log p_1 = A_1 - \frac{B_1}{T},$$

and

$$\log \frac{p}{p_1} = A - A_1 + \frac{B_1 - B}{T}.$$

Now for argon, krypton, and xenon respectively the values of A are 6·782, 6·972, and 6·963, and those of B are 339, 496·3, and 669·2 ; so that for these substances and many others $A - A_1$ is always a small quantity, while $\frac{B_1 - B}{T}$ is considerable and increases as T diminishes. Hence the ratio of p to p_1 increases rapidly as T diminishes, and by evaporating the gases always from the solid state and keeping the solid at as low a temperature as possible, the gas first removable at the lowest pressure consists in by far the greatest part of that which has the lowest boiling point, which in this case is nitrogen, and is succeeded, with comparative abruptness, by the gas which has the next higher boiling point. By this method the nitrogen and oxygen are removed without the necessity of sparking or absorption. The change from one gas to another is easily detected by examining the spectrum in the sparking tube, and the reservoirs into which the gases are pumped can be changed when the spectrum changes, and the fractions separately stored. Or, if several sparking tubes are interposed in such a way as to form parallel communications between the tubes b and e, any one of them can be sealed off at any desired stage of the fractionation.

The variation of the spectra of both xenon and krypton with variation in the character of the electric discharge is very striking, and has already been the subject of remark, in the case of krypton, by Runge, who has compared krypton with argon in its sensitiveness to changes in the electric discharge. Runge distinguishes krypton rays which are visible without a jar and those which are only visible with a jar discharge. The difference in the intensity of certain rays, according as the discharge is continuous or oscillatory, is no doubt very marked, but, with rare exceptions, we have found that the rays which are intensified by the oscillatory discharge can be seen with a continuous

discharge when the slit of the spectroscope is wide. Runge used a grating, whereas we have, for the sake of more light, used a prism spectroscope throughout, and were therefore able to observe many more rays than he.

There is one very remarkable change in the xenon spectrum produced by the introduction of a jar into the circuit. Without the jar xenon gives two bright green rays at about λ 4917 and λ 4924, but on putting a jar into the circuit they are replaced by a single still stronger ray at about λ 4922.* In no other case have we noticed a change so striking as this on merely changing the character of the discharge. Changes of the spectrum by the introduction of a jar into the circuit are, however, the rule rather than the exception, and there are changes in the spectrum of krypton which seem to depend on other circumstances. In the course of our examination of many tubes filled with krypton in the manner above indicated, we have found some of them to give with no jar the green ray λ 5571, the yellow ray λ 5871, and the red ray λ 7600 very bright, while other rays are very few, and those few barely visible. Putting a jar into the circuit makes very little difference; the three rays above mentioned remain much the brightest, nearly, though not quite, so bright as before, and the blue rays, so conspicuous in other tubes, though strengthened by the use of the jar, are still very weak. In other tubes the extreme red ray is invisible, the rays at λ 5571 and 5871 absolutely, as well as relatively, much feebler, while the strong blue rays are bright, even brighter than the green and yellow rays above named. In one tube the blue rays could be seen, though not the others. This looks very much as if two different gases were involved, but we have not been able to assure ourselves of that. The case seems nearly parallel with that of hydrogen. There are some hydrogen tubes which show the second spectrum of hydrogen very bright, and others which show only the first spectrum; the second spectrum is enfeebled or extinguished by introducing a jar into the circuit, while the first spectrum is strengthened; and the conditions which determine the appearance of the ultra-violet series of hydrogen rays have not yet been satisfactorily made out.

It is to be noted that putting the jar out of circuit does not in general immediately reduce the brightness of the rays which are strengthened by the jar discharge. Their intensity fades gradually, and is generally revived, more or less, by reversing the direction of the current, but this revival gets less marked at each reversal until the intensity reaches its minimum. The rays strengthened by the jar discharge also sometimes appear bright, without a jar, on first passing the spark when the electrodes are cold, and fade when the electrodes get hot, reappearing when the tube has cooled again. Moreover, if

* This line is almost identical with a strong helium line, but the yellow line of helium was not seen.

the discharge be continued without a jar, the resistance in the krypton tubes increases rather rapidly, the tube becomes much less luminous and finally refuses to pass the spark. With an oscillatory discharge the passage of the spark and the brightness of the rays are much more persistent. This seems to point to some action at the electrodes, which is more marked in the case of krypton than in that of xenon.

The wave-lengths of the xenon and krypton rays in the tables below were determined, in the visible part of the spectrum, with a spectroscope having three white flint-glass prisms of 60° each, by reference to the spark spectrum of iron, except in the cases of the extreme red ray of krypton, which was referred to the flame spectrum of potassium, and its fainter neighbour, which we saw but did not measure. The in digo, violet, and ultra-violet rays were measured in photographs, taken with quartz lenses and two calcite prisms of 60° each. The spectrum of the iron spark was photographed at the same time as that of the tube, the former being admitted through one-half of the slit, and the latter through the other half.

The xenon spectrum is characterised by a group of four conspicuous orange rays of about equal intensities, a group of very bright green rays of which two are especially conspicuous, and several very bright blue rays. The only list of xenon rays we have seen is that published by Erdmann, with which our list does not present any close agreement except as to the strongest green lines. The number of xenon rays we have observed is very considerable, and some of them lie very near to rays of the second spectrum of hydrogen, but inasmuch as these rays are more conspicuous with a jar in circuit than without, which is not the character of the second spectrum of hydrogen, and, moreover, many of the brightest of the hydrogen rays are absent from the spectrum of the tubes, we conclude that these rays are not due to hydrogen. Certain rays, which we have tabulated separately, have been as yet observed in only one tube: they include a very strong ultra-violet ray of unknown origin, and either due to some substance other than xenon, or to some condition of the tube which has not been repeated in the other tubes.

Our krypton rays agree much more closely with Runge's list, but outnumber his very considerably, as might be expected when prisms were used instead of a grating. Prisms, of course, cannot compete with gratings in the accuracy of wave-length determinations. We think that the krypton used by Runge must have contained some xenon, and that the rays for which he gives the wave-lengths 5419·38, 5292·37, and 4844·58 were really due to xenon, as they are three of the strongest rays emitted by our xenon tubes, and are weak in, and in some cases absent from, the spectra of our krypton tubes.

Our thanks are due to Mr. R. Lennox, to whose skill in manipula tion we are much indebted.

Tables of the approximate Wave-lengths of Xenon and Krypton Rays.

Rays observed only with a Leyden jar in circuit have an * prefixed, those observed only when no Leyden jar was in circuit have a † prefixed.

The intensities indicated are approximately those of the rays when a jar is in circuit, except in the case of the two rays to which a † is prefixed, which are not seen when a jar is in circuit. Rays which are equally intense whether a jar is in circuit or not have a || prefixed to the number indicating their intensities; those which are less intense with a jar than without have a < prefixed to the number expressing their intensities. The rest are, in general, decidedly more intense with a jar than without.

Xenon Rays.

Wave-lengths.	Intensity.	Wave-lengths.	Intensity.	Wave-lengths.	Intensity.	Wave-lengths.	Intensity.
*6596	4	5532	4	4883	—	4471	2
* 14	1	5473	3	76	4	62	10
6472	||1	61	3	44	10	49	6
6358	1	* 51	1	30	||1	40	1
45	3	39	3	23	3	34	2
20	||1	20	10	* 18	3	15	8
02	1	5372	6	07	<1	07	3
6278	3	* 68	1	4793	1	4396	4
71	3	39	6	87	2	93	4
6183	||1	13	1	79	2	86	3
81	||1	09	1	69	2	75	4
66	||1	5292	10	40	1	69	4
6097	6	62	2	34	<1	56	1
51	6	60	2	31	1	43	1
36	5	40	—	23	1	37	3
5976	6	27	1	14	1	31	10
72	—	02	1	4698	||3	22	3
46	2	5192	6	4677	band of	11	3
35	<1	89	3	to	close	4297	3
06	1	85	3	4668	lines	86	3
5895	||1	79	3	52	4	72	3
76	||1	26	3	34	2	69	3
56	||1	23	1	24	<2	63	2
25	2	07	3	16	3	51	3
17	—	5080	2	02	8	45	10
5777	4	68	5	4592	3	39	8
59	4	52	1	86	||5	27	1
51	5	45	6	77	3	23	5
27	4	25	<1	56	2	15	10
20	4	4988	4	45	3	14	6
00	6	72	2	41	3	09	8
5668	4	† 24	†4	35	2	04	||1
60	1	* 22	8	25	||5	01	1
17	—	† 17	†4	22	1	4198	1
09	1	4890	3	00	||1	93	||6
5583	1	87	—	4486	1	81	10
73	1	84	4	81	5	76	1

Xenon Rays—*continued*

Wave-lengths.	Inten-sity.	Wave-lengths.	Inten-sity.	Wave-lengths.	Inten-sity.	Wave-lengths.	Inten-sity.
4172	1	3981	1	3815	1	3655	2
63	3	75	1	11	3	50	1
59	3	73	2	07	1	45	6
46	3	57	||1	01	1	41	2
42	1	55	4	3792	1	32	2
32	2	51	<6	87	1	24	10
21	1	44	3	83	1	16	1
12	2	39	1	81	6	13	4
09	6	26	1	76	3	10	2
06	3	23	6	73	1	07	4
00	2	15	1	70	1	02	1
4099	3	08	4	66	1	3597	3
93	1	06	1	63	2	84	8
79	<1	03	1	62	1	80	8
74	1	3894	3	57	1	65	4
60	1	85	3	46	3	56	3
58	6	80	3	37	1	53	5
50	6	77	3	31	2	43	6
44	1	70	2	21	2	23	4
43	1	62	2	17	3	10	2
37	6	58	2	12	2	04	1
29	1	55	1	08	1	01	4
25	3	50	2	3689	1	3468	2
21	1	49	1	77	3	61	1
02	3	42	4	73	2	54	1
3994	2	29	1	64	1		
91	3	26	1	62	2		
86	1	24	1	58	1		

Wave-lengths of rays of unknown origin observed in the spectrum of one tube containing xenon but not present in the spectrum of other tubes :—

Wave-lengths.	Inten-sity.	Wave-lengths.	Inten-sity.
4589	—	3890	1
4071	1	72	1
67	1	3797	5
63	—	41	4
11	1	3684	10
3998	1	3573	2

Krypton Rays.

Wave-lengths.	Intensity.	Wave-lengths.	Intensity.	Wave-lengths.	Intensity.	Wave-lengths.	Intensity.
7600	8	5186	1	4387	3	3859	1
‡7587	2	72	1	76	3	58	1
6771	1	66	5	63	2	47	1
6578	1	43	4	56	12	44	2
42	3	26	6	23	2	42	1
11	2	5087	3	20	‖8	39	1
6487	3	78	1	19	‖3	37	2
58	<1	73	2	18	3	17	2
51	3	57	3	01	7	06	2
20	<4	34	1	4293	10	05	3
6305	3	23	4	83	‖3	3784	10
6170	2	14	‖2	74	‖4	79	8
6095	1	4980	1	69	3	72	4
82	1	60	1	60	1	59	2
56	2	46	1	56	1	55	6
21	1	03	2	51	5	46	6
11	2	4847	2	37	4	42	6
5992	3	45	2	4185	3	36	3
5873	1	* 33	5	72	1	34	4
71	<10	26	3	45	8	22	5
5771	2	12	3	40	2	19	10
53	2	4766	10	4119	3	15	1
5690	5	63	3	09	6	3691	1
82	5	39	10	4099	8	87	5
50	1	4694	3	89	8	81	7
32	2	80	5	65	7	70	7
5571	<10	59	8	58	6	67	1
63	3	50	1	45	4	64	3
53	1	35	6	38	2	61	3
44	1	20	8	08	2	54	10
23	2	15	6	05	1	49	3
06	2	10	3	3997	3	38	4
00	2	4598	1	94	6	32	10
5483	1	93	2	88	2	24	1
46	2	83	4	65	1	08	6
29	1	77	8	55	2	00	6
24	1	25	3	39	1	3590	3
03	1	05	‖2	28	3	74	1
5319	1	4490	2	21	8	54	2
05	1	75	6	18	2	45	6
5278	1	64	‖3 pairs	13	6	03	2
29	1	54	‖1	07	6	3489	2
18	1	37	6	01	1	70	1
15	1	32	6	3896	3	60	3
* 09	5	23	2	76	7		
03	1	00	1	62	1		

‡ This is taken from Runge's number for the wave-length, omitting the fraction.